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ELECTRICAL AND OPTICAL PROPERTIES OF In_2O_3 : Sn FILMS PREPARED BY ACTIVATED REACTIVE EVAPORATION*

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In_2O_3:Sn films were prepared by an activated reactive evaporation technique developed for this purpose. The films were characterized by transmission electron microscopy, electron diffraction, electrical resistivity and measurements of transmittance as a function of wavelength. The electrical resistivity is found to be strongly dependent on process parameters such as the tin content and the deposition temperature. In contrast, the transmittance is found to be only weakly dependent on various process parameters. Under optimum conditions, films with an electrical resistivity of 7×10^{-5} Ω cm with an integrated (0.4–1.2 μm) transmittance of over 90% were obtained.

INTRODUCTION

In_2O_3:Sn films are being increasingly used in the field of solar energy conversion. As these films are degenerate n-type semiconductors, they are used as a window material in heterojunction solar cells. Because of their high conductivity and high transparency in the visible part of the solar spectrum, these films are also used as a transparent contact for solar cells. In addition, they are used in solar photothermal conversion devices (as they have a high reflectance in the IR). Transparent conducting coatings of In_2O_3:Sn have been prepared by reactive sputtering from a metal alloy target[1–5] or by r.f. sputtering from an oxide target[6–10]. Although excellent coatings have been produced, these techniques have the disadvantage of high equipment cost and low deposition rates. Moreover, sputter-deposited coatings have invariably to be heat treated in a suitable ambient [11]. Other techniques such as spray pyrolysis[12] and chemical vapor deposition[13] have also been used with varying degrees of success. Pyrolytically deposited films have a high degree of internal stresses[11] as these are prepared by spraying onto glass substrates heated to temperatures as high as 400–800 °C.

Recently, Nath and Bunshah[14] have used a modified activated reactive evaporation technique for deposition of high quality In_2O_3 and In_2O_3:Sn films. The technique essentially involves resistive evaporation of indium or an In–Sn alloy in

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the presence of a reactive ambient. The reaction between the evaporating species and the gas is activated by establishing a thermionically assisted plasma in the reaction zone. The films can be deposited at rates as high as 0.05 μm min^{-1} and preparation involves no post-deposition treatment. In this paper we report on the properties of these films and their dependence on deposition conditions such as substrate temperature and tin concentration in the alloy.

2. EXPERIMENTAL DETAILS

The experimental apparatus used for deposition of the films has been described earlier. A resistively heated tungsten source is used to evaporate indium or In–(0–20 wt.%) Sn onto chemically cleaned glass and quartz substrates in the presence of Ar–15%O_2. The films were deposited onto substrates maintained at temperatures ranging from 25 to 400 °C. The deposition rate was 0.04 μm min^{-1}. The pressure during deposition was maintained at 1×10^{-4} Torr. In order to enhance the reactivity of the indium or In–Sn vapor species with the reaction gas, a dense plasma was generated in the reaction zone by employing a thoriated tungsten emitter and a low voltage anode assembly.

The microstructure and the crystallographic structure of the films were analyzed by X-ray diffraction, transmission electron microscopy (TEM) and electron diffraction (the specimens for TEM studies were deposited on KCl crystals and the films were floated off). The sheet resistance and the electrical resistivity were measured by a conventional four-probe arrangement. The optical transmittance was measured as a function of wavelength between 0.3 and 1.8 μm.

3. RESULTS

The sheet resistance as a function of tin concentration in the In–Sn alloy for films deposited at 300 °C is shown in Fig. 1. It is seen that the sheet resistance decreases rapidly with increasing tin concentration up to 18 wt.% Sn in the In–Sn

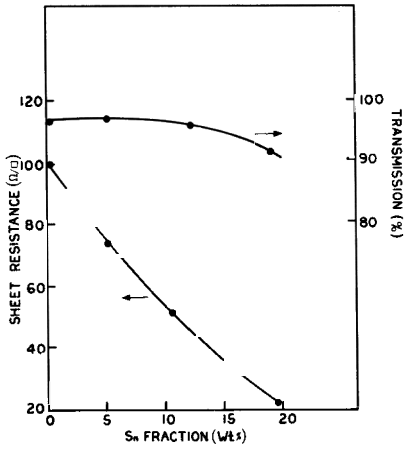

Fig. 1. Plots of the sheet resistance and the integrated (0.4–1.2 μm) transmittance against the tin concentration (in the In–Sn alloy) for In_2O_3:Sn films. The deposition temperature is 300 °C.

alloy. Beyond 20 wt.% Sn, good quality films could not be obtained. The integrated (0.4–1.2 μm) value of the transmittance for these films is also given in Fig. 1. It should be noted that whereas the sheet resistance is a strong function of tin content the transmittance is only weakly dependent on it. These results indicate that the optimum tin concentration in the alloy for obtaining the lowest sheet resistance and highest figure of merit[15], T^{10}/R_s, is approximately 15–18 wt.%. It may be pointed out that the exact role of tin in determining the properties is far from clear. The optimum tin content has been found to be different (from a few per cent up to 20 wt.%) by different workers[11,15] in films prepared by different techniques.

The electrical resistivity of In_2O_3:Sn films, with tin concentrations of 18 wt.% in the In–Sn alloy, as a function of deposition temperature is shown in Fig. 2. The electrical resistivity decreases monotonically with an increase in the temperature of deposition up to 250 °C. Beyond 250 °C the electrical resistivity decreases very rapidly. The integrated (0.4–1.2 μm) transmittance for these films is also shown in Fig. 2. It is seen that whereas the electrical resistivity is a strong function of the substrate temperature the transmittance is only weakly dependent on it. It may be pointed out that all In_2O_3:Sn films deposited at temperatures ranging from 50 to 370 °C exhibit sharp optical absorption edges.

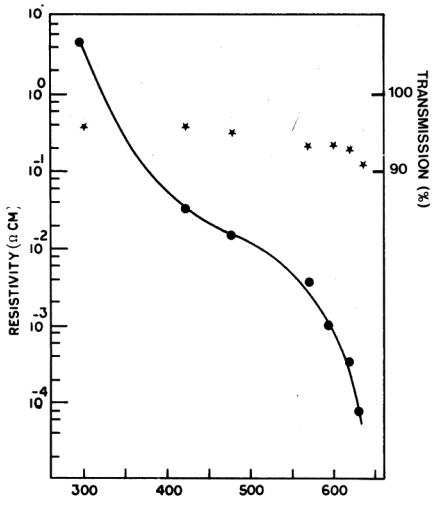

Fig. 2. Plots of the electrical resistivity (●) against the deposition temperature for In_2O_3:Sn (18 wt.% Sn in the alloy) films. The integrated (0.4–1.2 μm) transmittance (*) is also shown.

The temperature dependence of the electrical resistivity of In_2O_3:Sn (with a tin concentration of 18 wt.% in the alloy) films deposited at deposition temperatures ranging from room temperature to 370 °C is shown in Fig. 3. It is seen that the films deposited at room temperature show a semiconducting behavior with an activation energy for conduction which decreases with a decrease in temperature. The activation energy of conduction is between 0.015 and 0.027 eV, indicating the shallow nature of the doping levels. With an increase in deposition temperature, the resistivity dependence on temperature becomes weaker. Beyond 150 °C the resistivity behavior changes; instead of decreasing with temperature it increases

with temperature. Hall effect studies indicate that the electrical conductivity is n type and the films have a Hall mobility of 20–30 $cm^2\ V^{-1}\ s^{-1}$ and a carrier concentration of approximately $10^{21}\ cm^{-3}$.

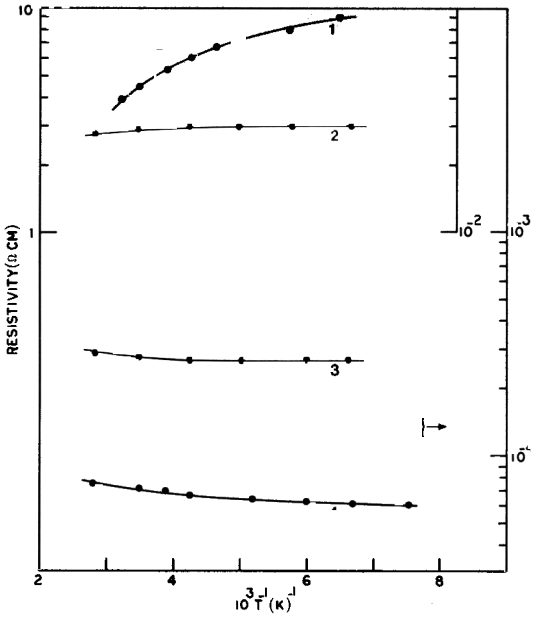

Fig. 3. Inverse temperature dependence of the electrical resistivity of In_2O_3:Sn (18 wt.% Sn in the alloy) films deposited at different temperatures: curve 1, 23 °C; curve 2, 150 °C; curve 3, 350 °C; curve 4, 370 °C.

The observed dependence of the electrical resistivity on deposition temperature can be understood qualitatively in terms of (1) oxygen vacancies and (2) the microstructure and crystallinity of the deposits. Lower deposition temperatures lead to stoichiometric oxide films. This is indicated by the sharp absorption edge and the high degree of transparency in the wavelength range 0.4–1.2 μm. Increasing the deposition temperature leads to oxygen-deficient films. The oxygen vacancies thus created are responsible for the higher conductivity. This is well known in the literature[11,15]. The effect of deposition temperature on the crystallinity and microstructure is shown in Fig. 4. It is seen that films deposited at room temperature have no discernible microstructure. The films exhibit a broad halo diffraction pattern. Increasing the deposition temperature results in highly crystalline films with crystallite size increasing with increasing temperature of deposition. This is indicated by the electron diffraction patterns which also show preferred orientation. X-ray diffraction studies have also shown (111) preferred orientation in these films[14].

4. CONCLUSION

We showed that activated reactive evaporation can be used to deposit In_2O_3:Sn films of high optical quality at temperatures ranging from room temperature to 370 °C. The electrical properties depend sensitively on the temperature of deposition and the tin content.

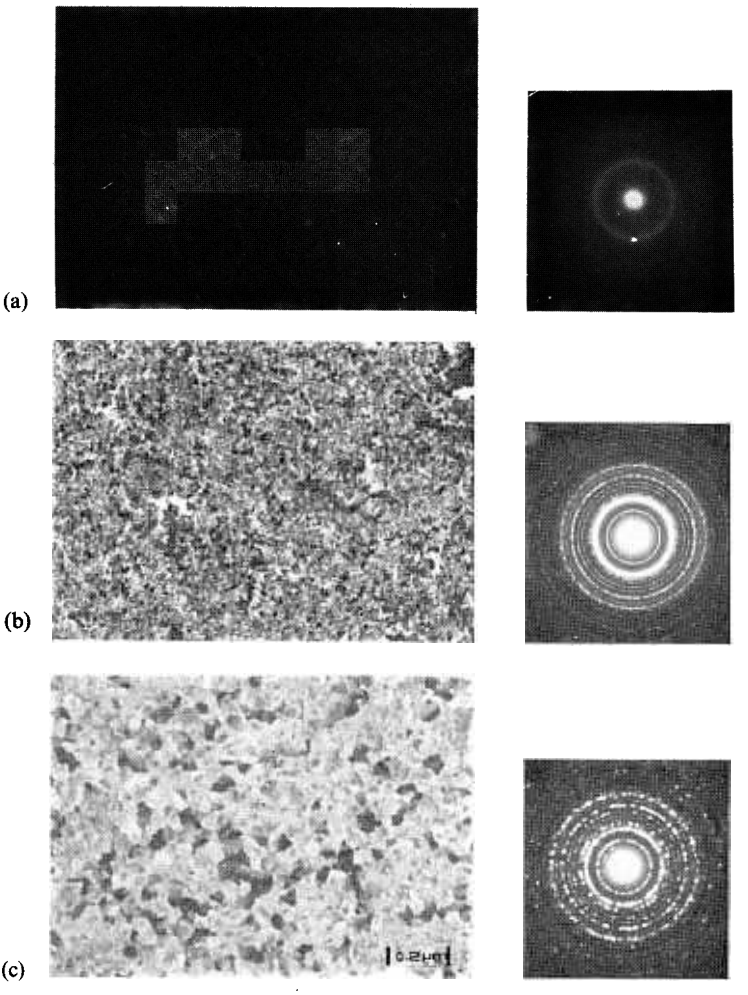

Fig. 4. TEM micrographs and electron diffraction patterns for In_2O_3:Sn films: (a) at 23 °C; (b) 250 °C; (c) 370 °C.

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